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Application of Nonlinear Transformations to the Evaluation of Multicenter Integrals

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The evaluation of multicenter integrals is necessary for *ab initio* calculations. Expansion techniques give infinite series which must be summed. We have used several nonlinear sequence-to-sequence transformations to obtain more rapidly convergent series. The best of these transformations reduces the time necessary to evaluate some four-center integrals by as much as 75%. This transformation improved the convergence of all of the twenty integrals we have treated.

INTRODUCTION

MOLECULAR systems of increasing complexity are becoming amenable to *ab initio* calculations. One of the major difficulties preventing the extension of these techniques to larger systems is the computer time necessary to evaluate multicenter integrals. Except in the smallest molecules, most of the computer time necessary to do a calculation is spent evaluating these integrals.

The troublesome molecular integrals are of the form

$$I=\iint \chi_{A_1}{}^{(1)}(1)\chi_{A_2}{}^{(2)}(1)F(1,2)\chi_{A_3}{}^{(3)}(2)\chi_{A_4}{}^{(4)}(2)dv_1dv_2$$

$$=\langle\chi_{A_1}{}^{(1)}\chi_{A_2}{}^{(2)}\mid F\mid\chi_{A_3}{}^{(3)}\chi_{A_4}{}^{(4)}\rangle, \quad (1)$$

where $\chi_{A_j}{}^{(j)}$ (1) is basis function j centered on Nucleus A_j, as a function of the space coordinates of Electron 1, and $F(1,2)$ is a function of the coordinates of both electrons. They are referred to as one-, two-, three-, or four-center integrals according to whether four, three, two, or none of the A_j's are the same. The basis functions are usually of the Slater type

$$\chi(j)=N(n,l,m)r_j{}^{n-1}\exp(-\beta r_j)P_l{}^m(\cos\theta_j)\exp(im\phi_j), \quad (2)$$

where r_j, θ_j, and ϕ_j are the spherical coordinates of Electron j and the $P_l{}^m$ are Legendre polynominals. For convenience we assume that n is less than 3. The β's are usually chosen to minimize the energy. Several methods of evaluating these integrals have been proposed.[1] The Gaussian transform method is very efficient,[1] especially if the Aitken δ^2 transformation[2,3] is used to accelerate convergence. However, this method does not work well if two or more basis functions have widely different exponents.[1] The most popular method is the zeta-function method[1] which is based on the expansion[4]

$$r_{A_i}{}^{n_j-1}\exp(-k_jr_{A_j})=\sum_{i_j=0}^{\infty}\frac{(2i_j+1)}{(r_{A_j}\rho_{A_j})^{1/2}}P_{i_j}(\cos\theta_{A_j})\zeta_{n_j,i_j}(k_j,r_{A_1};\rho_{A_j}), \quad (3)$$

where ρ_{A_j} is the distance from A_1 to A_j. Prosser and Shull[1b] have commented that this widely used method suffers from a relatively slow convergence. We discuss some sequence-to-sequence transformations which substantially improve the efficiency of the zeta-function method. The zeta-function method involves the expansion of the integrand about one or two centers. We only consider the single-center zeta-function expansion method, although the general approach we use could be applied to any expansion procedure.

THEORY AND RESULTS

The zeta functions with $n_j=0$ are obtained as products of modified Bessel functions of half-integer order. The zeta functions with $n_j>0$ are then obtained by the use of recursion relations. Barnett[5] gives an excellent detailed discussion of the zeta-function method. Expansion of the exponential functions on Centers A_2, A_3, and A_4 about Center A_1 leads to a triply infinite series if A_2, A_3, and A_4 are all different from A_1. We then substitute $l=\frac{1}{2}(i_2+i_3+i_4)$ to obtain the series

$$I=\sum_{l=0}^{\infty}\{\sum_{i_2=0}^{2l}\sum_{i_3=0}^{2l-i_2}f(i_2,i_3,2l-i_2-i_3)\}$$

$$=\sum_{i_2=0}^{\infty}\sum_{i_3=0}^{\infty}\sum_{i_4=0}^{\infty}f(i_2,i_3,i_4), \quad (4)$$

which is a simple infinite series in the index l. The Nth partial sum, I_N, is defined as

$$I_N\equiv\sum_{l=0}^{N}\{\sum_{i_2=0}^{2l}\sum_{i_3=0}^{2l-i_2}f(i_2,i_3,2l-i_2-i_3)\}. \quad (5)$$

The forward difference operator, Δ, is defined by

$$\Delta I_N\equiv I_{N+1}-I_N, \quad (6)$$

* NSF Summer Fellow.

† Contribution No. 3472.

[1] (a) I. Shavitt, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. 2; (b) F. Prosser and H. Shull, Ann. Rev. Phys. Chem. **17**, 51 (1966).

[2] A. C. Aitken, Proc. Roy. Soc. Edinburgh **46**, 289 (1926).

[3] A. C. Aitken, Proc. Roy. Soc. Edinburgh **57**, 269 (1937).

[4] C. A. Coulson, Proc. Cambridge Phil. Soc. **33**, 104 (1937).

[5] M. P. Barnett in Ref. 1.

where $I_{-1}\equiv 0$. The evaluation of the functions, f, in Eq. (5) is very time consuming and the double summation causes the evaluation of the sequence $\{I_N\}$, to become progressively more difficult for large N. Figure 1 shows the average time required to evaluate several three- and four-center integrals from ethane as a function of the number of terms used. We can save a great deal of time by reducing the number of terms required to give the desired accuracy. The most straightforward estimate of the value of the integral is to use I_N for some large N. This approach assumes that we have no knowledge of the truncation error

$$\epsilon_N \equiv I - I_N = \sum_{l=N+1}^{\infty} \Delta I_{l-1}. \tag{7}$$

More efficient methods make use of the available knowledge of this error. In order to be useful such a method must give a reliable estimate of the truncation error for some N less than the N originally required for the desired accuracy. In Appendix A we show that the asymptotic form of the single-center zeta-function expansion series for all multicenter integrals is

$$I_a = \sum_{l=M}^{\infty} \{ \sum_{j=1}^{n} a_j \cos(l\theta_j + \alpha_j) \lambda_j^l l^{-m_j/2} \}, \tag{8}$$

where $\lambda_j \leq 1$ and n is finite. We use this asymptotic form to develop a method of estimating the truncation error and show that the method leads to a considerable reduction in the computer time required to evaluate these multicenter integrals.

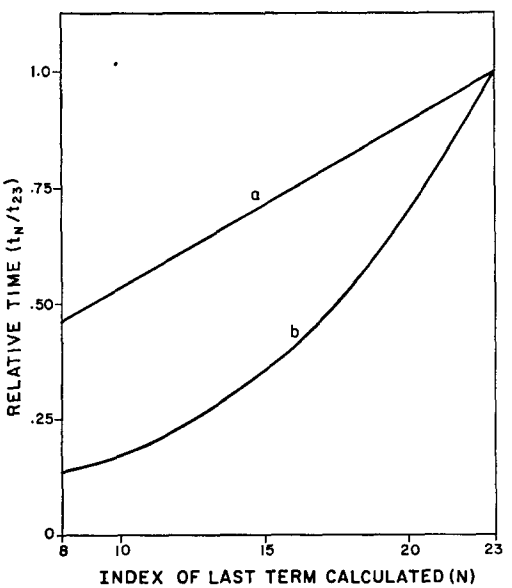

FIG. 1. The relative time required to calculate partial sum I_N as a function of N. The first curve, a, is the average for several three-center integrals such as $\langle \chi_A^{(1)} \chi_B^{(2)} \mid r_{12}^{-1} \mid \chi_A^{(3)} \chi_C^{(4)} \rangle$. The second curve, b, is the average for several four-center integrals, $\langle \chi_A^{(1)} \chi_B^{(2)} \mid r_{12}^{-1} \mid \chi_C^{(3)} \chi_D^{(4)} \rangle$, with various basis functions. These curves demonstrate that considerable time could be saved by reducing the number of terms evaluated in the series expansion.

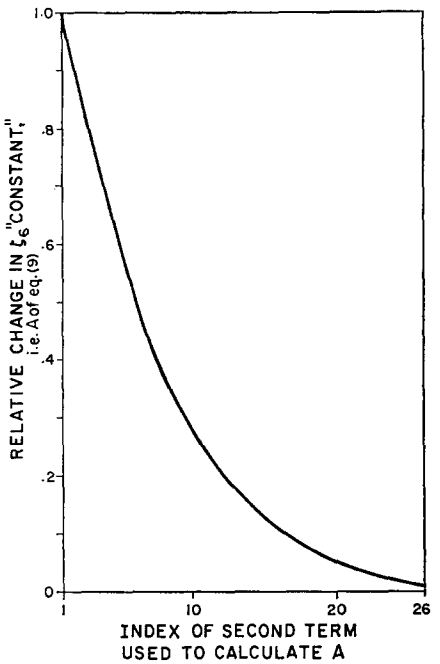

FIG. 2. The relative change in A, [of Eq. (9)], $\Delta A_N/A_{N+1}$, as a function of N for a two-center exchange integral taken from calculations on formaldehyde. Since this relative change is much less than one for small N, the asymptotic form, Eq. (9), is a good approximation for the series expansion of this integral.

The simplest multicenter integral is the two-center exchange integral, $\langle \chi_A^{(1)} \chi_B^{(2)} \mid r_{12}^{-1} \mid \chi_A^{(3)} \chi_B^{(4)} \rangle$, for which $\theta_j = 0$, $\lambda_j = 1$, and $m_j = 12$ in Eq. (8). This means that asymptotically we have

$$I \doteq I_N + \sum_{l=N+1}^{\infty} A l^{-6}, \tag{9}$$

where A is independent of N for large N. In order to use this form to estimate the truncation error we must determine A. Subtracting the analogous expression for I_{N-1} from Eq. (9) gives

$$\Delta I_{N-1} \equiv I_N - I_{N-1} \doteq A N^{-6}, \tag{10}$$

which defines A as a function of the terms of the infinite series. We define a sequence of "*local constants*" $\{A_N\}$ where A_N is calculated from I_N and I_{N-1} by Eq. (10). If the sequence $\{I_N\}$ is nearly of the form given in Eq. (9) then the A_N should vary only slightly. In Fig. 2 we show the relative change in A_N, $\Delta A_N/A_{N+1}$, as a function of N for a two-center exchange integral taken from calculations on formaldehyde. The sequence $\{A_N\}$ is nearly constant for small N and it is reasonable to use the asymptotic form, Eq. (9), to estimate the truncation error ϵ_N [see Eq. (7)]. We now have the estimate for the truncation error,

$$\epsilon_N \doteq N^6 \Delta I_{N-1} [\zeta(6) - \sum_{l=1}^{N} l^{-6}], \tag{11}$$

where $\zeta(6)$ is the Riemann zeta function. We use the

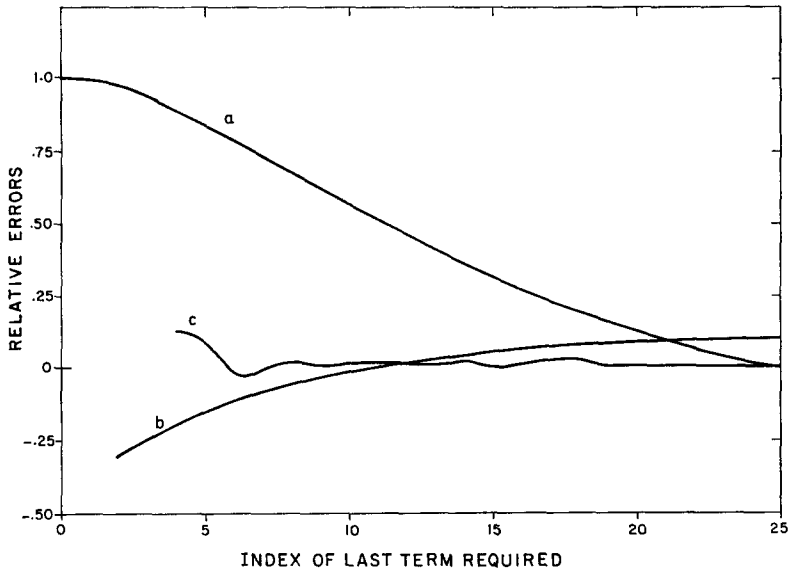

FIG. 3. The relative errors for transformations of the sequence of partial sum approximations to the series expansion for the integral [see text above Eq. (11)] as a function of the number of terms required for the transformation. The relative error is the error after the transformation divided by the error before the transformation. Curve a is the relative error for the ζ_6 transformation [Eq. (12)]. Curve b is the relative error for the e_1 transformation [Eq. (14)]. Curve c is the relative error for the $\tilde{e}_d$ transformation [Eqs. (17)–(19)]. All three transformations accelerate convergence.

value of $\zeta(6)$ to define the ζ_6 transformation of the sequence $\{I_N\}$,

$$\zeta_6(I_N) \equiv I_N + N^6 \Delta I_{N-1} \left[\frac{\pi^6}{945} - \sum_{l=1}^{N} l^{-6} \right] \quad (12)$$

which forms a new sequence $\{\zeta_6(I_N)\}$ that converges to I for a two-center exchange integral. For large N the error in the new sequence $[I-\zeta_6(I_N)]$ is much smaller than the corresponding error in the original sequence ϵ_N since the ζ_6 transformation was derived using the asymptotic form of the two-center exchange integral. This transformation is useful only if the ratio of these errors, $[I-\zeta_6(I_N)]/\epsilon_N$, is much less than 1 for small N. Figure 3 shows this ratio as a function of N for the integral from formaldehyde used above. The required condition is met and ζ_6 is a useful transformation for two-center exchange integrals.

A second interesting transformation is due to Aitken[2,3] and is based upon the assumption

$$I = I_N + Aq^N \quad (13)$$

for the truncation error, where A is the "*amplitude*" and q is the "*ratio*." The ratio is less than 1 for a convergent sequence. This defines the e_1 transformation,

$$e_1(I_N) \equiv I_N + [(1/\Delta I_N) - (1/\Delta I_{N-1})]^{-1} \quad (14)$$

in the same way that Eq. (9) defines the ζ_6 transformation. The e_1 transformation is frequently called the Aitken δ^2 process. In Appendix B we show that the application of the e_1 transformation to the Riemann zeta function gives a new sequence which converges monotonically and more rapidly than the original sequence to $\zeta(6)$. The ζ_6 transformation of the Riemann zeta function gives the exact limit immediately. However, Fig. 3 indicates that for small N the e_1 transformation is more accurate than the ζ_6 transformation of a two-center exchange integral.

A generalization of the e_1 transformation is discussed in great detail by Shanks.[6] Typical convergent sequences include both monotonic and oscillatory types. Multicenter integrals offer abundant examples of both types. If we draw a smooth curve through the discrete points of a graph of I_N vs N, this graph looks like a stable physical transient for either of the above types of sequences. This suggests the possibility of approximating the truncation error of multicenter integrals by a mathematical transient

$$I = I_N + \sum_{j=1}^{k} A_j q_j^N, \quad (15)$$

where the transient is of "*order*" k, with "*amplitudes*"

TABLE I. A three-center Coulomb integral from a calculation on H_2O.

Index of last term required N	Approximate values[a] for the integral $\times 10^5$: Sum of the first N terms I_N[b]	Transformation of order 2, $e_2(I_{N-2})$[c]	Transformation of maximum order $\tilde{e}_d(I_N)$[d]
0	253.7340		253.7340
3	66.1983		−134.2630
6	−95.1562	7.7023	12.9940
9	−68.7839	1.0640	0.1091
12	−22.6435	0.1474	0.1851
15	−1.6678	0.2007	0.1908
18	3.2419	0.2184	0.1877
21	2.6270	0.2027	0.1877
24	1.2068	0.1907	0.1878
27	0.3088	0.1866	0.1878
28	0.6712	0.1904	0.1878
29	−0.1008	0.1875	0.1878

[a] The correct value of this integral is 0.187624×10^{-5} which was obtained by expanding about a different center.
[b] See Eq. (5).
[c] See Eqs. (17) and (18).
[d] See Eq. (19).

[6] D. Shanks, J. Math. Phys. **34**, 1 (1955).

A_j, and "*ratios*" q_j. This equation defines the e_k transformation in the same way that Eq. (9) defined the ζ_6 transformation and Eq. (13) defined the e_1 transformation. We can solve Eq. (15) for I and for A_j and q_j $(j=1, k)$ if we know I_N for $2k+1$ values of N. Solution of this system of equations for I leads to the transformation

$$e_k(I_N)\equiv\frac{\begin{vmatrix} I_{N-k} & \cdots & I_{N-1} & I_N \\ \Delta I_{N-k} & \cdots & \Delta I_{N-1} & \Delta I_N \\ \Delta I_{N-k+1} & \cdots & \Delta I_N & \Delta I_{N+1} \\ \cdot & & \cdot & \cdot \\ \cdot & & \cdot & \cdot \\ \cdot & & \cdot & \cdot \\ \Delta I_{N-1} & \cdots & & \Delta I_{N+k-1} \end{vmatrix}}{\begin{vmatrix} 1 & \cdots & 1 & 1 \\ \Delta I_{N-k} & \cdots & \Delta I_{N-1} & \Delta I_N \\ \Delta I_{N-k+1} & \cdots & \Delta I_N & \Delta I_{N+1} \\ \cdot & & \cdot & \cdot \\ \cdot & & \cdot & \cdot \\ \cdot & & \cdot & \cdot \\ \Delta I_{N-1} & \cdots & & \Delta I_{N+k-1} \end{vmatrix}} \tag{16}$$

which is a ratio of two determinants of dimension k. This is very time consuming to evaluate. Fortunately, Wynn[7] has developed an efficient algorithm for these transformations. He defines the intermediate quantities g_m as

$$g_{2m}(I_N)\equiv e_m(I_N),$$
$$g_{2m+1}(I_N)\equiv 1/e_m(\Delta I_N), \tag{17}$$

and shows that

$$g_{m+1}(I_N)=g_{m-1}(I_{N+1})+[g_m(I_{N+1})-g_m(I_N)]^{-1} \tag{18}$$

for any m greater than zero. In particular, we choose the transformation

$$\tilde{e}_d(I_{2N})\equiv e_N(I_N),$$
$$\tilde{e}_d(I_{2N+1})\equiv e_N(I_{N+1}), \tag{19}$$

which uses the highest-order transient possible for all N. This transformation has been applied to the two-center exchange integral treated previously and the results are given in Fig. 3. This is the most powerful of the three transformations we have used.

Treatment of the simple Riemann zeta function by the e_1 transformation involves the approximation

$$l^{-m/2}\doteq(N+1)^{-m/2}\{[N/(N+1)]^{m/2}\}^{l-N-1}, \quad (l>N), \tag{20}$$

as shown in Appendix B. Applying this approximation to the general asymptotic form for a multicenter integral [Eq. (8)] gives

$$I\doteq\sum_{l=M}^{N}\Delta I_l+\sum_{l=N+1}^{\infty}\left\{\sum_{j=1}^{n}a_jN^{-m_j/2}\left[\left(\frac{N+1}{N}\right)^{m_j/2}\right]^N \times\cos(l\theta_j+\alpha_j)\left[\left(\frac{N}{N+1}\right)^{m_j/2}\lambda_j\right]^l\right\} \tag{21}$$

as the approximate asymptotic form. The truncation error is therefore

$$\epsilon_N\doteq\sum_{l=N+1}^{\infty}\{\sum_{j=1}^{n}b_j\cos(l\theta_j+\alpha_j)\mu_j{}^l\}=\sum_{j=1}^{k}A_jq_j{}^l, \tag{22}$$

where k is finite. This fits into the scheme of the e_k transformation with the q_j occurring in complex conjugate pairs. The $\tilde{e}_d$ transformation will eventually accelerate the convergence of any multicenter integral.

We have applied the Wynn algorithm to several multicenter integrals. The $\tilde{e}_d$ transformation gives a consistently accurate estimate of the truncation error. Table I gives a dramatic example of the improvement we have achieved with this transformation. The method is most effective with the most slowly convergent series, such as the example in Table I. Table II gives the results for a typical four-center integral. Although this example is not as spectacular as the previous one, the $\tilde{e}_d$ transformation still gives a marked improvement in the convergence. The more rapidly convergent series such as the example given in Table II show little improvement when the $\tilde{e}_d$ transformation is substituted for the simpler e_2 transformation. The e_2 transformation is important because it is the simplest transformation based on transients which can show an oscillatory behavior for the truncation error.

We checked the program for the Wynn algorithm[7] by comparing the e_2 transformation with the algorithm developed by Aitken[2,8] which is based on a similar asymptotic form but is completely independent. The two agreed to within 1 ppm. The Wynn algorithm is

TABLE II. A four-center integral from a calculation on C_2H_6.

Index of last term required N	Approximate values for the integral $\times 10^5$		
	Sum of the first N terms I_N	Transformation of order 2 $e_2(I_{N-2})$	Transformation of maximum order $\tilde{e}_d(I_N)$
0	3.134678		3.134678
3	1.099399		0.144892
6	0.664420	0.629253	0.631534
9	0.630630	0.632112	0.632648
12	0.630873	0.632438	0.632455
15	0.631958	0.632452	0.632454
18	0.632337	0.632453	0.632454
21	0.632433	0.632454	0.632454
22	0.632446	0.632454	0.632454
23	0.632465	0.632454	0.632454

[7] P. Wynn, Math. Aids Computation **54**, 91 (1956).

[8] A. C. Aitken, Proc. Roy. Soc. Edinburgh **A63**, 174 (1951).

TABLE III. The $\tilde{e}_d$ transformation of some four-center integrals from C_2H_6.

Integral	Relative error after $\tilde{e}_d$ transformation[a]	Relative truncation error[b]$\times 10^6$	$\lvert I-\tilde{e}_d(I_{12})\rvert/\lvert\epsilon_{23}\rvert$[c]
$\langle 1s_A 1s_B \mid r_{12}^{-1} \mid 1s_C 1s_D\rangle$	0.046	17	3.0
$\langle 1s_A 1s_B \mid r_{12}^{-1} \mid 1s_C 1s_D\rangle$	0.050	340	1.6
$\langle 2s_A 1s_B \mid r_{12}^{-1} \mid 1s_C 1s_D\rangle$	0.0083	17	0.46
$\langle 2s_A 1s_B \mid r_{12}^{-1} \mid 1s_C 1s_D\rangle$	0.031	370	1.0
$\langle 2p_{z_A} 1s_B \mid r_{12}^{-1} \mid 1s_C 1s_D\rangle$	0.0093	14	0.36
$\langle 2p_{z_A} 1s_B \mid r_{12}^{-1} \mid 1s_C 1s_D\rangle$	0.00051	2 500	0.071
$\langle 2p_{z_A} 1s_B \mid r_{12}^{-1} \mid 1s_C 1s_D\rangle$	0.0063	51	1.0
$\langle 2p_{x_A} 1s_B \mid r_{12}^{-1} \mid 1s_C 1s_D\rangle$	0.00044	2 000	0.29
$\langle 2p_{y_A} 1s_B \mid r_{12}^{-1} \mid 1s_C 1s_D\rangle$	0.0064	52	1.1
$\langle 2p_{y_A} 1s_B \mid r_{12}^{-1} \mid 1s_C 1s_D\rangle$	0.00064	180 000	0.29

[a] Since the relative error $\lvert I-\tilde{e}_d(I_{12})\rvert/\lvert\epsilon_{12}\rvert$ is much less than one, the $\tilde{e}_d$ transformation gives considerable acceleration of convergence.

[b] Since the relative truncation error $\lvert\epsilon_{12}/I\rvert$ is greater than 10^{-6}, the improved accuracy is important.

[c] The error for the $\tilde{e}_d$ transformation of the first 13 terms is roughly the same as the error for the first 24 terms without any transformation. Therefore we have reduced the number of terms required by a factor of 2.

slightly unstable for high-order transformations because it requires finding small differences between large numbers, but the use of double-precision arithmetic eliminates this problem.

We have summarized the results of the application of the $\tilde{e}_d$ transformation to 10 four-center integrals in Table III. In most cases $\tilde{e}_d(I_{12})$ gives all available information about the value of the integral. The round-off error in summing ΔI_N and the error in the numerical quadrature used to calculate ΔI_N prevent accuracy greater than six significant figures. This accuracy is usually achieved with $\tilde{e}_d(I_{12})$. The relative error for this transformation, $[I-\tilde{e}_d(I_{12})]/\epsilon_{12}$, is listed for the 10 integrals in Table III. Our estimate for the truncation error is on the average accurate to within 1%. The third column in the table indicates that the truncation error is large enough so that this improvement is important. The final column indicates that the error in the transformed sequence after 13 terms, $I-\tilde{e}_d(I_{12})$, is comparable to the error in the original sequence after 24 terms, ϵ_{23}. We have reduced the number of terms required for a given accuracy by about a factor of 2. The time required to carry out the transformation is negligible compared to the time required to compute additional partial sums. From Fig. 1 we see that the time required to evaluate these four-center integrals has been reduced by about 75%. Additional three- and four-center integrals were treated and gave results similar to those reported above.

CONCLUSIONS

Expansion techniques used to evaluate multicenter integrals give rise to infinite series which must be summed. We have used the asymptotic forms of these series to develop sequence-to-sequence transformations which accelerate convergence. The Wynn[7] algorithm provides an efficient method of obtaining rapidly convergent sequences for multicenter integrals. The application of the $\tilde{e}_d$ transformation to the first 13 partial sums usually provides six significant figures accuracy for the sum of the series. This is the maximum accuracy possible if the partial sums are computed in single-precision arithmetic. This transformation reduces the time necessary to evaluate four-center integrals by as much as 75%. Although we have restricted this discussion to the zeta-function expansion of basis functions with principal quantum number less than three, the basic approach is quite general.

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APPENDIX A: ASYMPTOTIC FORMS OF MULTICENTER INTEGRALS

Sahni and LaBudde[9,10] have derived the asymptotic forms of single-center zeta-function expansions for all integrals of interest except the four-center electron repulsion integral. We give a brief description of their method and indicate the differences which arise in the four-center case. The complexity of the four-center

[9] R. C. Sahni and C. D. LaBudde, J. Chem. Phys. **33**, 1015 (1960).

[10] C. D. LaBudde and R. C. Sahni, J. Chem. Phys. **33**, 1022 (1960).

TABLE IV. The asymptotic forms of two- and three-center integrals.

Integral						Asymptotic form		
Name	A_1	A_2	A_3	A_4	$F(1,2)$	Restriction	λ	ν
Two-center exchange integral	A	B	A	B	r_{12}^{-1}	None	1	6
Three-center potential-energy integral	A		B		r_{c1}^{-1}	$\rho_B<\rho_C$	(ρ_B/ρ_C)	2
						$\rho_B>\rho_C$	(ρ_C/ρ_B)	2
						$\rho_B=\rho_C$	1	3
Three-center exchange integral	A	B	A	C	r_{12}^{-1}	$\rho_B<\rho_C$	(ρ_B/ρ_C)	4
						$\rho_B>\rho_C$	(ρ_C/ρ_B)	5
						$\rho_B=\rho_C$	1	6
Three-center Coulomb integral	B	B	A	C	r_{12}^{-1}	$\rho_B<\rho_C$,[a]	(ρ_B/ρ_C)	5
						$\rho_B>\rho_C$,[a]	(ρ_C/ρ_B)	6
						$\rho_B=\rho_C$,[a]	1	7
						$\rho_B<\rho_C$,[b]	(ρ_B/ρ_C)	4
						$\rho_B>\rho_C$,[b]	(ρ_C/ρ_B)	5
						$\rho_B=\rho_C$,[b]	1	6

[a] $\chi_B^{(1)}(1)=\chi_B^{(2)}(1)=$Slater $2s$ orbital. [b] Case a is not true.

case requires the use of several questionable approximations to obtain the asymptotic form.

We first expand the potential function r_{12}^{-1} and the Legendre polynomials at Centers A_2, A_3, and A_4 about Center A_1. Then we expand the remaining terms, $r_{A_i}^{n_i}\exp(-k_j r_{A_j})$, about Center A_1 using the zeta-function expansion of Coulson.[4] The spherical harmonics are then rotated so that they are all in one coordinate system (with A_1–A_2 as the z axis) and the θ and ϕ integrations are carried out. In the four-center case we cannot carry out the θ integration exactly, but instead we use the approximation

$$P_l^m(\cos\theta)\doteq[\Gamma(l+m+1)/\Gamma(l+\tfrac{3}{2})](\tfrac{1}{2}\pi\sin\theta)^{-\frac{1}{2}} \times\cos[(l+\tfrac{1}{2})\theta-\tfrac{1}{4}\pi+m\tfrac{1}{2}\pi], \quad \text{(A1)}$$

which reduces the θ integrals to a simple form. The function Γ is just the gamma function. We obtain the asymptotic form of the radial integrals from a series of inequalities given by Sahni and LaBudde. In the four-center case we have a triply infinite series over the indices i_2, i_3, and i_4. We introduce the index $l=\frac{1}{2}(i_2+i_3+i_4)$ and sum the resulting finite series over indices i_2 and i_3 using approximations such as

$$\sum_{i_3=l-i_2}^{l}(l+i_3)^{-1}\lambda^{i_3}\cos(i_3\theta) \doteq 2(4l-i_2)^{-1}\sum_{i_3=l-i_2}^{l}\lambda^{i_3}\cos(i_3\theta), \quad \text{(A2)}$$

where we have used the average value of i_3 for the slowly varying part of the expression. This approximation is quite good when i_2 is small compared to l, but can be very bad for large i_2.

The resulting asymptotic form of two- and three-center integrals is

$$I_a=\sum_{l=M}^{\infty} l^{-\nu}\lambda^l\sum_{j=1}^{k}K_j P_{l+\tau_j}(\cos\Theta_c), \quad \text{(A3)}$$

where Θ_c is the angle formed by Centers B, A, and C. The specific cases studied by Sahni and Labudde are summarized in Table IV. We now use the approximation for $P_{l+\tau_i}(\cos\Theta_c)$ given by Eq. (A1) to obtain the asymptotic form

$$I_a=\sum_{l=m}^{\infty}\left\{\sum_{j=1}^{k}\frac{a_j\cos(l\theta_j+\alpha_j)\lambda_j^l}{l^{m_j/2}}\right\}, \quad \text{(A4)}$$

which is also the approximate asymptotic form of the four-center electron repulsion integral. In the four-center case, the λ_j take on such values as $(\rho_<^2/\rho_-\rho_>)$, $(\rho_-/\rho_>)$, and $(\rho_</\rho_-)$, where $\rho_<$ is the smallest, ρ_- is the intermediate, and $\rho_>$ is the largest of the ρ_{A_j}. We now have a convenient general asymptotic form for single-center zeta-function expansions of multicenter integrals.

APPENDIX B: THE e_1 TRANSFORMATION OF THE RIEMANN ZETA FUNCTION

The transformation of this simple sequence provides valuable insight into the effect of comparable transformations on more complicated sequences. The Riemann zeta function $\zeta(n)$ is the limit of the sequence $\{S_N\}$ where

$$S_N=\sum_{l=1}^{N}l^{-n} \quad \text{(B1)}$$

as N approaches infinity. Application of the e_1 transformation, Eq. (14), gives the new sequence

$$e_1(S_N)=S_N+(N+1)^{-n}\{1-[N/(N+1)]^n\}^{-1}, \quad \text{(B2)}$$

where the correction term involves the sum of a

geometric series. Therefore $e_1(S_N) > S_N$ and the e_1 transformation makes the approximation

$$\epsilon_N \doteqdot (N+1)^{-n} \sum_{j=0}^{\infty} \left[\left(\frac{N}{N+1}\right)^n\right]^j \tag{B3}$$

for the truncation error of the Riemann zeta function. The exact truncation error is

$$\epsilon_N = \sum_{j=0}^{\infty} (N+j+1)^{-n}. \tag{B4}$$

To compare Eq. (B3) with Eq. (B4) we multiply the numerator and denominator of the terms in Eq. (B4) by N^{jn}. This gives

$$(N+j+1)^{-n} = \{N^j/[N^{j+1} + (j+1)N^j]\}^n, \tag{B5}$$

where the denominator is the first two terms in the expansion of $(N+1)^{j+1}$. This leads us to the approximation

$$(N+j+1)^{-n} = \{N^j/[(N+1)^{j+1}]\}^n[1+O(j^2/N^2)], \tag{B6}$$

where the term $O(j^2/N^2)$ is positive. Therefore

$$(N+j+1)^{-n} = (N+1)^{-n}\{[N/(N+1)]^n\}^j[1+O(j^2/N^2)] \tag{B7}$$

which is the desired connection between Eqs. (B3) and (B4). The approximation of the truncation error given by Eq. (B3) is asymptotically correct. The transformed sequence increases monotonically to the limit $\zeta(n)$, and

$$S_N < e_1(S_N) < \zeta(N). \tag{B8}$$

We shall find the approximation, Eq. (B7), especially useful.

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Series Expansion for Two-Center Noninteger-n Overlap Integrals*

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A series in the internuclear distance R is derived for the two-center overlap integral between noninteger-n Slater-type orbitals. There are in general two types of terms: $R^{2N+\lambda}$ and $R^{n_1+n_2+1+N}$, $(N=0,1,2,\cdots;$ $\lambda=|l_1-l_2|, |l_1-l_2|+1, \cdots, l_1+l_2)$. When n_1+n_2 is an integer while n_1 and n_2 are not integers, logarithmic terms arise. The series is for general values of n_1, n_2, l_1, l_2, m_1, m_2, ζ_1, and ζ_2, and it converges absolutely for $R<\infty$.

INTRODUCTION

TWO-CENTER overlap integrals with noninteger-n Slater-type atomic orbitals (STO) were reduced to a one-dimensional integration by the Fourier-transform convolution theorem in an earlier paper.[1] In this paper the final integration is expressed as a series in the internuclear distance R. The series is valid for general values of n_1, n_2, l_1, l_2, m_1, m_2, ζ_1, ζ_2, and $\mathbf{R}$. When n_1+n_2 is nonintegral, the series consists of two types of terms: a power series and $R^{n_1+n_2}$ times a power series. The series becomes an ordinary power series when both n_1 and n_2 are integers. When neither n_1 nor n_2 is an integer while n_1+n_2 is, there are logarithmic terms.

For the reader interested only in the working results, see Eqs. (7), (32), (33), (37), and (41).

FORMULATION

The overlap integral between a STO at the origin, characterized by the parameters n_1, l_1, m_1, ζ_1, and a STO at $\mathbf{R}$ with parameters n_2, l_2, m_2, ζ_2, is given by [Eq. (16) of I]

$$S_{n_1 l_1 m_1 \zeta_1; n_2 l_2 m_2 \zeta_2}(\mathbf{R}) = N_{n_1\zeta_1} N_{n_2\zeta_2} (2\pi^2)^{-1} \sum_{\lambda=|l_1-l_2|}^{l_1+l_2} c^{\lambda}(l_2, m_2; l_1, m_1)(2\lambda+1)^{1/2}(4\pi)^{-1/2} Y_{\lambda}^{m_2-m_1}(\theta_R, \phi_R) i^{\lambda}$$
$$\times \int_0^{\infty} dk\, k^2 f^*_{n_1 l_1 \zeta_1}(k) f_{n_2 l_2 \zeta_2}(k) j_{\lambda}(kR). \tag{1}$$

(A complete explanation of the symbols and conventions can be found in I.) Briefly, the $N_{n\zeta}$ are normalization

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[1] H. J. Silverstone, J. Chem. Phys. **45**, 4337 (1966), hereafter referred to as I.